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A NEW SEPARATION OF THORIUM

FROM

CERIUM, LANTHANUM AND DIDYMIUM

AND ITS APPLICATION TO

THE ANALYSIS OF MONAZITE

By

FLOYD J. METZGER, PH. B.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY

NEW YORK CITY

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INTRODUCTION.

The marked disagreement, among well recognized chemists, in the determination of thorium in monazite sand, seemed sufficient to warrant a more careful investigation of the methods now existing for its determination, and it was with this object in view that the following work was undertaken.

By thorium, is meant the element as it was generally understood before the more recent researches of Brauner and Baskerville which point quite conclusively toward the isolation of a new element from what is now generally called thorium.

F. J. M.

ACKNOWLEDGMENT.

This investigation was carried out under the direction of Professor Edmund H. Miller and I wish here to express my most sincere thanks to him for his kind interest and encouragement in the work, and for the valuable assistance rendered.

F. J. M.

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May 1, 1902.

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A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.

Review of Methods.

Among the methods proposed for the separation and purification of thorium, the following may be mentioned as the more important.

Ammonium oxalate Separation.

Bahr* was the first to notice that thorium oxalate was soluble in a hot concentrated solution of ammonium oxalate. R. Bunsen † applied this solubility in ammonium oxalate for a separation of thorium from the other rare earths, and showed that by reprecipitation, thorium could be completely isolated from the associated rare earths.

Later investigators made various modifications of Bunsen's method: namely—C. Glaser ‡ says that the addition of a little ammonium acetate to the ammonium oxalate makes the thorium oxalate more soluble, and thus affects a more complete separation. In the same paper he states that by acidifying the solution of thorium in ammonium oxalate, with hydrochloric acid, the thorium is reprecipitated quantitatively.

Whether thorium oxalate, after its solution in hot concentrated ammonium oxalate, remains soluble after cooling and dilution, was for some time a matter of uncertainty. Hintz and Weber,§ however, after a very careful study of this point, say that thorium oxalate is completely soluble in a hot concentrated solution of ammonium oxalate, and that the solution remains clear after cooling, dilution, and even after two days standing.

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* *Lieb. Ann.* (1864) 132–231.

† Pogg. Ann. (1875) 155–380.

‡ *Zts. Anal. Chem.* (1897) 36, 213.

§ *Zts. Anal. Chem.* (1897) 36, 27.

Also that if a hot solution (slightly acid) of thorium nitrate (or chloride) is treated with a hot concentrated solution of ammonium oxalate, a clear solution is obtained which remains clear after cooling, dilution, and after standing for several days.

The same workers (H. & W.) also investigated the addition of ammonium acetate to the ammonium oxalate as proposed by Glaser, and find that this addition of ammonium acetate has no influence whatever on the separation.

Brauner * has made a comparative research on the oxalates of the rare earths, and sums up his work as follows:

(a) The solubility of the oxalates of the earths of the cerium and yttrium groups in ammonium oxalate is very small as compared with that of thorium oxalate.

(b) The oxalate of lanthanum, as that of the most positive or basic of all the known rare earths, is dissolved to the smallest extent, whereas that of the most negative (thorium) is very easily dissolved.

(c) The tendency to form double or complex oxalates decreases with increasing basicity of the rare earths.

(d) Thorium is distinguished from the trivalent earth metals by the considerably smaller solubility of its oxalate in mineral acids.

Thiosulphate Separation.

The separation of thorium from the other rare earths by using thiosulphate was first proposed by Chydenius † and later worked by Hermann, ‡ Drossbach, § Hintz and Weber, ‖ and others.

The separation is based on the fact that thorium is precipitated from a neutral or slightly acid solution, by sodium thiosulphate, while cerium and the other rare earths remain in solution.

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* *Jour. Lond. Chem. Soc.* (1898), 73, 972.
† Pogg. Ann. 119, 46.
‡ *Jour. f. präkt. Chem.* 93, 106.
§ *Ztsch. angew. Chem.* (1901), 655.
‖ *Ztsch. Anal. Chem.* (1897), 36, 676; *Ztsch. Anal. Ch.* 35, 525.

As was pointed out by Chydenius * and also Glaser, † the precipitation is not complete in one operation, but by reprecipitating the filtrate with ammonia, converting this into the chloride and reprecipitating with sodium thiosulphate (repeating as long as a precipitate is obtained with sodium thiosulphate), a complete separation is obtained.

Hintz and Weber ‡ say the separation works best in dilute solutions and in the presence of two or three drops of dilute hydrochloric acid. They, (H. & W.), give this method preference.

Hydrogen peroxide Separation.

Cleve § was the first to show that thorium could be precipitated by hydrogen peroxide from a sulphate solution, and that the precipitate had the composition represented by the formula $Th_4O_7SO_3$.

Boisbaudran ‖ also used hydrogen peroxide as a precipitant about the same time.

Wyrouboff and Verneuil ¶ carried the investigation a little farther and showed that an analagous precipitate of thorium could be obtained from a solution of the nitrate (i. e. $Th_4O_7N_2O_5$) and that it gave a complete separation of thorium from the other rare earths.

Kosmann ** separated the greater part of the didymium salt from the crude material, as sulphate. Then he separated thorium from cerium, lanthanum and didymium by successive treatment of the acid solution with hydrogen peroxide solution; an acid-ammonium citrate solution, and ammonia. A precipitate of aluminium phosphate and thorium hydrate was formed which was afterwards separated by oxalic acid.

* Loc. cit.
† *Chem. Ztg.* (1896), 20, 612.
‡ Loc cit.
§ Bull. Soc. Chim. (1885), 43, 53.
‖ C. R. 100, 605.
¶ C. R. (1898), 126, 340.
** Central Bladt (1897), pt. 1, 837.

Acetyl-acetone Method.

Urbain* used acetyl-acetone to prepare an absolutely pure thorium salt. The thorium was first separated by using a hot concentrated solution of ammonium oxalate. This solution was then precipitated with an excess of ammonia (instead of an acid), and the hydrate suspended in dilute alcohol. To this he added acetyl-acetone and evaporated to dryness on a water bath. On taking this up with chloroform, the thorium acetyl-acetonate [Th $(C_5H_7O_2)_4$] was dissolved, which, on slow evaporation was deposited in well defined crystals and was free from any other rare earths.

Sodium Sulphite Method.

A separation, based on the fact that from a neutral solution of the rare earths, sodium sulphite precipitates all except thorium which remains in solution, was proposed by Chavastelon.† The author states that the thorium thus obtained is not quite pure, but that subsequent purification is then quite easy, using hydrogen peroxide.

Cuprous Oxide Separation.

Boisbaudran‡ precipitates thorium by means of cuprous oxide after the cerium has been reduced by copper turnings and hydrchloric acid, in the following way:

Add to the solution of the rare earths, slightly acid with hydrochloric acid, some pure copper turnings. This reduces the cerium to the cerous salt. Then add to this solution a large excess of cuprous oxide and boil. The thorium is precipitated and can be filtered off while the other rare earths except a trace of cerium go into the filtrate. The thorium thus obtained must be submitted to a second or third treatment to free it entirely from cerium. The filtrate containing the cerium is also likely to contain thorium and needs to be retreated. The combined thorium precipitates

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* Bull. Soc. Chim. (1896), 15, 347.

† C. Bldt. (1900), 1, 876.

‡ *Chem. News* (1884), 50, 201, also C. R. 1884, 99, 525–6.

are then freed from copper by any of the ordinary methods (hydrogen sulphide or ammonia in excess).

Nitride Separation.

Dennis * separates thorium from its associated rare earths by using potassium nitride. The precipitation is made in a solution very faintly acid with nitric acid. It is necessary to have the solution quite dilute, and a current of air passed through the liquid during precipitation, aids the process.

† His conversion of the oxalates into nitrates is a very lengthy one, consisting of the solution of the ignited oxides in nitric acid which requires digestion on a water-bath with concentrated nitric acid for one and one-half to two days.

Separation of Thorium from Zirconium by the Use of Potassium-acid-Fluoride.

Delafontaine ‡ isolates zirconium from thorium and the other rare earths by fusion with acid potassium fluoride. The powdered ore is fused with twice its weight of the fluoride. The zirconium is dissolved as potassium fluo-zirconate (K_2ZrF_6) out of the solidified mass by means of boiling water containing a few drops of hydrofluoric acid. The insoluble fluorides, decomposed by sulphuric acid and ignited below a dull red heat will leave thorium, cerium and the other rare earths as sulphates, which are dissolved in water, and the thorium separated by the ammonium oxalate method already outlined. The zirconium is thrown down from its fluo-salt by ammonia.

Potassium Chromate as a Precipitant for Thorium.

Muthmann and Baur § used potassium chromate as a precipitant to prepare pure thoria. 840 grams of thorium nitrate of commerce were dissolved in five litres of water, and steam,

* *Am. Ch. Jour.* (1894), 16, 79, and again J. A. C. S. (1896), 18, 947.
† Note by author.
‡ *Chem. News.* (1897), 75, 230.
§ Ber. (1900), 33^2, 2028.

under three atmospheres pressure, was passed in while one litre of a six per cent. solution of potassium chromate was slowly dropped in. This operation had to be repeated six times. The combined precipitates of thorium chromate [$Th(CrO_4)_2$] from the various fractions gave 320 grams of pure white oxide of thorium. Then by further precipitation there was obtained a dirty olive-green chromate; and out of the remaining, from which potassium chromate would give no further precipitate, gadolinium and yttrium were precipitated by caustic potash. About one-half gram of oxides of gadolinium and yttrium were obtained.

Method based on Solubility of Oxides.

As early as 1839 Kersten * proposed a method for separating thorium from cerium, based upon the difference of their solubility in hydrochloric acid. After igniting the salts to the oxides, hydrochloric acid was added, and the cerium easily dissolved, while only traces of thorium went into solution. He says the separation is not sharp, but gives a proximate estimation.

Purification of Thorium by Precipitating the Hydrated Sulphate.

Nilson † purified thorium by first evaporating to dryness with sulphuric acid, thus forming the anhydrous sulphate, which was then projected into water at O° C and gently warmed to about 10° C. The hyrated sulphate of thorium containing 9 H_2O, which is quite insoluble separated out and was filtered off. The filtrate was again evaporated to dryness with sulphuric acid and treated in the same way. This was repeated until $Th(SO_4)_2$ $9H_2O$ no longer separated out on warming, giving a pure thorium salt, while the impurities remained in solution.

Cleve modified Nilson's process, in that instead of evaporating each time with sulphuric acid, he precipitated the filtrate

* Pogg. Ann. (1839), 47, 385.

† Berichte (1882), 2521; also Ber. (1887) 1666.

with ammonia, filtered, dissolved in hydrochloric acid, then added sulphuric acid and evaporated to dryness. This gave a much smaller bulk to evaporate, and he says that after three treatments of this kind he obtained thorium absolutely free from cerium and didymium.

Complete Analysis of Monazite.

Undoubtedly the best method which has yet been published for the complete analysis of monazite is that of Glaser. *

Comparison of Methods.

Benz † in a recent article, makes a very careful study of the methods now employed for the analysis of monazite (the ammonium oxalate, thiosulphate and hydrogen peroxide methods) and gives a good comparison of their accuracy.

He finds that one digestion of the mixed oxalates with even a large excess of ammonium oxalate is insufficient to bring into solution all the thorium; on the contrary he finds that only about one-half the thorium is dissolved, and that after repeated digestions considerable cerium is brought into solution.

With the thiosulphate method he gets very good results after three or four precipitations, and obtains the thoria almost without a trace of cerium. This, however, has the disadvantage of being extremely long.

Hydrogen peroxide, as he shows, precipitates thorium completely from a neutral solution, or from a solution very faintly acid with nitric acid. It also separates thorium from cerium and lanthanum by one reprecipitation.

EXPERIMENTAL.

Various Precipitants Tried.

In view of the fact that very few weak organic acids have hitherto been employed for the separation of thorium from its associated rare earths, the following were tried:

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* *Jour. Am. Ch. Soc.* (1896), 18, 789.

† Zeit. angew. Ch. (1902), 297.

Maleic acid: Aqueous solutions of maleic acid with thorium, cerium, lanthanum and didymium give no preciptate hot or cold. Solutions of cerium, lanthanum and didymium in 50% alcohol give nothing hot or cold.

A solution of thorium in 50% alcohol, gives no precipitate in the cold, but on heating, a partial precipitation results.

Cinnamic acid produces at least a partial precipitation of thorium from 20% alcoholic solutions. The precipitate cannot be filtered (runs through) and for this reason the completeness of the precipitation was not determined. Cerium, lanthanum and didymium give nothing under the same conditions.

Picric acid and thorium, in alcoholic solutions, give a partial precipitation of thorium. Cerium, lanthanum and didymium give no precipitate under these conditions.

Phthalic acid in aqueous solution with cerium, lanthanum and didymium gives nothing cold or hot. Thorium, however, in aqueous solution with phthalic acid gives a partial precipitation on heating. From alcoholic solutions a heavy curdy precipitate results on heating, and is approximately half complete.

Cerium, lanthanum and didymium in alcoholic solutions with phthalic acid give no preciptate.

Fumaric acid: Aqueous solutions, hot or cold, give nothing with cerium, lanthanum or didymium.

Thorium and Fumaric acid in aqueous solutions give a precipitate in the cold, which forms slowly, but on applying heat the precipitate forms rapidly, (white, floculent) settles out nicely, and is almost complete. From solution in 95% alcohol, fumaric acid precipitates thorium quantitatively even in the cold.

Cerium and fumaric acid in 95% alcohol give no precipitate in the cold, but on heating, a small fraction of the cerium is thrown down. Lanthanum and didymium in 95% alcohol give nothing cold or hot. From solutions in 40% alcohol fumaric acid gives a quantitative precipitation of thorium on heating; lathanum and didymium under the same conditions give nothing. Cerium in 40% alcohol gives, with fumaric acid, nothing cold or hot, unless the cerium solution is quite strong, when a very small fraction is precipitated.

Ammonium fumarate precipitates thorium, cerium, lanthanum and didymium from aqueous solutions, insoluble in excess, soluble in mineral acids.

Among the amido compounds tried were:

Urea gave nothing.

Thio urea gave nothing.

Acetamide " "

Semicarbazide gave nothing.

Succinimide gives no precipitation of cerium, but gives a partial precipitation or thorium from alcoholic solutions.

Diethyl-amine precipitates thorium, cerium, lathanum and didymium.

The Quantitate Precipitation of Thorium by Fumaric Acid.

From the experiments given on a preceding page it was now evident that thorium could be precipitated quantitatively from alcoholic solutions, leaving cerium, lanthanum and didymium in solution.

It was desirable to know the smallest quantity of alcohol necessary to affect this precipitation, and still leave the cerium, lanthanum and didymium in solution. This strength was reached when the solution contained 40% of alcohol.

The following results will show the completeness of the precipitation from the various strengths of solution:

		ThO_2	
% alcohol.	volume.	taken.	found.
15	150 c.c.	0.1568	0.1508
35	150	0.1568	0.1551
40	200	0.1961	0.1962
40	150	0.1568	0.1561
40	120	0.1176	0.1176
40	120	0.2007	0.2003
40	100	0.1004	0.1006
40	120	0.1176	0.1179
40	200	0.1961	0.1962

Separation of Thorium from Cerium, Lanthanum and Didymium.

The salts used for the experiments were the best nitrates that could be purchased, and the thorium nitrate was purified according to the method suggested by Wyrouboff and Verneuil* which is as follows:

Eighty-three grams of the nitrate, corresponding approximately to thirty-nine grams of thoria, were dissolved in eight litres of water. The solution was divided equally in twelve beakers and precipitated with hydrogen peroxide (10 c.c. H_2O_2 for every 0.5 gr. ThO_2). The solutions were then heated to 85° C and allowed to settle. The precipitates were washed a dozen times by decantation with hot water, and then transferred to a large Büchner funnel and the washing continued until the filtrate gave no precipitate with ammonia. The precipitate was then transferred to a large porcelain evaporating dish and 150 c.c. of concentrated nitric acid added; heat was applied and the whole went into solution readily. The solution was evaporated to dryness, taken up in water, diluted to eight litres, and the process repeated.

The filtrate from the hydrogen peroxide precipitation was treated with ammonia and hydrogen peroxide, giving a brown precipitate of CeO_3. This precipitate of peroxide of cerium was examined for lanthanum and didymium, but none could be detected.

A stock solution was made of this purified thorium nitrate and standardized very carefully by precipitation with oxalic acid. This was the thorium used for the experiments.

A cold saturated solution of fumaric acid in 40% alcohol (containing approximately 0.1 gr. per 10 c.c.) was used as the precipitant.

Method of Analysis.

Make the solution of the neutral nitrate 40% alcohol (volume about 150-175 c.c. with 0.1-0.2 gr. ThO_2 and about same amount of admixed oxides), then add 12-15 c.c. of fumaric acid solution

*C. R. (1898), 126, 4, 340.

(about 0.10 gr. per 10 c.c.) for each 0.1 gr. ThO_2 and heat to boiling (75°-80°C); allow to stand a few minutes until the precipitate settles, then filter, while still hot, through a long stem funnel, or by suction. Wash the precipitate four or five times with hot 40% alcohol, then put paper and precipitate into a platinum crucible, ignite and weigh as ThO_2.

A number of analyses were made in this way using mixtures of thorium with cerium, lanthanum and didymium and it was found that the thorium invariably carried with it an appreciable quantity of the impurity which could not be washed out, nor could it be prevented by the addition of such salts as NH_4Cl, NH_4NO_3, &c.

A few results will show the extent to which these impurities are carried down.

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid.	Volume.	ThO_2 taken.	ThO_2 found.
0.2000			25 c.c.	150 c.c.	0.1725	0.1730
0.2000			"	"	0.1961	0.1982
	0.2000		"	"	0.1921	0.1941
	0.2000		"	"	0.1961	0.1990
	0.2000		"	"	0.1882	0.1907
	0.2000		"	"	0.1961	0.1978
		0.2000	"	"	0.1961	0.1992
		0.2000	"	"	0.1961	0.1972
		0.2000	"	"	0.1882	0.1901
		0.2000	"	"	0.1961	0.1979

Reprecipitation was next tried, and gave very satisfactory results. For this reprecipitation it is only necessary to dissolve the preciptate of thorium fumarate (formed by the first precipitation) off the filter in hot dilute hydrochloric acid—or better, place the paper and precipitate back into the beaker, add a little dilute hydrochloric acid, heat, then filter off the paper—and evaporate to dryness on a water bath. During the process of this evaporation some of the salt adheres to the sides of the beaker, but this is easily obviated by shaking the beaker occasionally and washing down with a few drops of water from a wash-bottle.

When the residue is free from acid (better add a few cubic centimeters of water and evaporate a second time), add about

50 c. c. water (leaving the beaker on the water bath) and stir the residue loose from the bottom with a rubber capped stirring rod; some carbonaceous matter from the fumaric acid, partly decomposed, and also some fumaric acid and a trace of thorium fumarate will remain insoluble at this point, but need not be regarded. Add alcohol sufficient to make the solution 40%, dilute to the proper volume with 40% alcohol, add a little fumaric acid (8-10 c.c.) and precipitate as before; wash, ignite and weigh.

Hydrochloric acid was used instead of nitric for the solution of the thorium fumarate, for the reason that nitric acid formed, on evaporation, a deposit which was practically insoluble in water.

The following results will show the accuracy of the separation:

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid.	Volume.	ThO_2 taken.	ThO_2 found.
0.2000			25 c c.	150 c.c.	0.1961	0.1966
0.2000			"	"	0.1961	0.1957
	0.2000		"	"	0.1961	0.1964
	0.2000		"	"	0.1961	0.1959
		0.2000	"	"	0.1961	0.1965
		0.2000	"	"	0.1968	0.1965

Mixtures of thorium, cerium, lanthanum and didymium were then made in the proportions in which they are usually found in monazite sand, and analyzed the same as above with these results:

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid.	Volume.	ThO_2 taken.	ThO_2 found.
0.283	0.133	0.157	10 c c.	175 c.c.	0.0557	0.0558
0.283	0.133	0.157	25 "	200 "	0.0572	0.0571
0.283	0.133	0.157	10 "	175 "	0.0572	0.0574
0.283	0.133	0.157	10 "	175 "	0.0557	0.0558
0.566	0.266	0.314	15 "	350 "	0.1115	0.1114
0.566	0.266	0.314	15 "	350 "	0.1129	0.1132

Mixtures containing equal amounts of thorium, cerium, lanthanum and didymium, and mixtures containing thorium in excess were then analyzed as follows:

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid.	Volume.	ThO_2 taken.	ThO_2 found.
0.1000	0.1000	0.1000	10 c.c.	120 c.c.	0.0995	0.0990
0.1000	0.1000	0.1000	10 "	120 "	0.1003	0.0995
0.1000	0.1000	0.0000	25 "	130 "	0.1529	0.1523
0.1000	0.1000	0.1000	40 "	150 "	0.2007	0.2002
0.1000	0.1000	0.1000	40 "	150 "	0.2015	0.2010
0.1000	0.1000	0.1000	60 "	150 "	0.3011	0.3005
0.1000	0.1000	0.1000	60 "	150 "	0.3019	0.3023
0.0500	0.0500	0.0500	25 "	200 "	0.1961	0.1963
0.0500	0.0500	0.0500	25 "	200 "	0.1968	0.1969
0.0250	0.0250	0.0250	25 "	200 "	0.1976	0.1971
0.0250	0.0250	0.0250	25 "	200 "	0.1991	0.1985

Effect of Salts With Acetic Radicles on the Precipitation of Thorium by Fumaric Acid.

A very peculiar effect is noticed when a salt, containing an acetic radicle, is added to a solution of the rare earths (Ce, La. Di., &c.) which has already had added to it some fumaric acid. The results are these:

Take a solution of cerium (La or Di) in 40% alcohol and add to it a solution of fumaric acid; nothing results. If now, one or two drops of ammonium acetate is added to this mixture of cerium and fumaric acid, the cerium is precipitated completely. Then if to this solution containing the precipitate an excess of ammonium acetate is added, the whole redissolves and leaves a clear solution.

Cerium (La or Di) is not precipitated by ammonium acetate alone.

Ammonium fumarate precipitates cerium (La or Di) insoluble in excess of precipitant.

Add to cerium (La or Di) dissolved in 40% alcohol, fumaric acid, and then one or two drops of acetic acid, and nothing results; but then by adding to this one or two drops of ammonium acetate, the cerium is thrown down quantitatively as before.

Thorium differs from cerium, lathanum and didymium in that the precipitate formed by fumaric acid is only partially soluble in an excess of ammonium acetate.

Sodium acetate has the same effect as ammonium acetate.

The exact reaction in the above experiments has not yet been studied, but it is quite evident that salts of acetic acid must be avoided in the separation of thorium from cerium, lanthanum and didymium by fumaric acid.

The Effect of Other Metals on the Separation.

It was very desirable to know the effect of other metals on the precipitation of thorium by fumaric acid, so all the metals available were tried. The solutions in all cases (where such solutions could be obtained) were made in 40% alcohol and the fumaric acid added. The following salts were tried:
$CuSO_4$; $AgNO_3$; $AuCl_3$ (acid); $MgCl_2$; $CaCl_2$; $Sr(NO_3)_2$; $BaCl_2$; $ZnSO_4$; $CdCl_2$; $Hg_2(NO_3)_2$; $Hg(NO_3)_2$; $HgCl_2$; H_3BO_4; $Na_2B_4O_7$; Al_2Cl_6; $SnCl_4$ (acid); $SnCl_2$ (acid); $Pb(NO_3)_2$; $MnCl_2$; Na_2HPO_4; As_2O_3 (slightly sol.); Sb (tartar emetic); $Bi(NO_3)_3$ (slightly sol.); Ur (acetate); Vd (chloride); Na_2WO_4; Fe_2Cl_6; $FeSO_4$; $CoCl_2$; $NiCl_2$; Ir & Pt (chlorides).

Of the above named salts, $AgNO_3$; $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ were the only ones which gave any precipitation. The precipitation of mercurous nitrate appears quantitative as well as the precipitation of mercuric nitrate, while mercuric chloride gives no precipitate whatever. The precipitation of silver nitrate is only a partial one.

Among the rare earths obtainable were yttrium, samarium, gadolinium, erbium and zirconium, which, dissolved in 40% alcohol gave with fumaric acid:

Yttrium gives no precipitate cold or hot.

Samarium " " " " " "

Gadolinium " " " " " "

Erbium gives a very slight precipitate in the cold, which seems to increase somewhat on heating. Only a very small fraction, however, is thrown down.

Zirconium gives a quantitative precipitation on heating.

The Composition of the Precipitate Formed by Thorium and Fumaric Acid.

To determine the composition of the thorium fumarate, a quantity of pure salt was prepared by precipitating the purified thorium solution with fumaric acid, washing very thoroughly with 40% alcohol and drying. The salt was first dried at 105° C in an air bath, and then to determine the point at which the salt was decomposed, the temperature was gradually raised causing a gradual loss in weight until at 202°-205° C it became practically constant and no indications of decomposition were evident even at 245°-247° C. This dried salt, however, reabsorbed moisture to a considerable extent when exposed to the air. The loss on heating is:

Weight of air-dried salt				= 0.4085
2½ hrs.	@	105° C	loss	= 0.0669
1 "	longer	"	"	= .0000
2¾ "	"	@ 122°	"	= .0010
3 "	"	" "	"	= .0006
2 "	"	" "	"	= .0000
4 "	"	" 142°-145°	"	= .0010
1½ "	"	" " "	"	= .0000
3 "	"	" 160°-163°	"	= .0004
2½ "	"	" " "	"	= .0000
2½ "	"	" 184°-187°	"	= .0006
2½ "	"	" " "	"	= .0000
4 "	"	" 202°-205°	"	= .0003
1½ "	"	" " "	"	= .0000
1½ "	"	" 222°-225°	"	= .0000
1½ "	"	" 245°-247°	"	= .0002

In order to obtain concordant results, the water was first driven off at 105° C, collected and weighed as atmospheric moisture. For this purpose a large tin can, provided with a thermometer, was placed upon the combustion furnace, and the tube passed through in the reverse position. Air was passed through the tube and the temperature maintained at 105° for four hours; the absorption tube weighed, the can removed and

the combustion made in a current of oxygen. The water obtained in this was calculated as water of composition. The residue left in the boat should be thoria, and was weighed as such.

A number of combustions made in the above manner gave no constant results for hydrogen, while the thorium-carbon ratio was practically 1 : 4 as is seen from these results:

	ThO_2	CO_2	*Ratio*
I	0.1319	0.0883	1 : 4.01
II	0.1606	0.1086	1 : 4.05

The above ratios were calculated from the thoria just after removal from the furnace.

After the combustion had been completed and the boat (containing the thoria) weighed, it was placed in a platinum tube and heated with a blast lamp for ten or fifteen minutes. White fumes were given off, and the thoria decreased in weight to the extent of several milligrams. These fumes do not condense, but if made to pass through alcohol they are partially absorbed, and from this solution a very slight precipitate can be thrown down with ammonia. Some of the losses which occurred after combustions of this sort are:

0.1606 gr.	thoria	lost	on	ignition	0.0039 gr.
0.1147 "	"	"	"	"	0.0036
0.1403 "	"	"	"	"	0.0053
0.1641 "	"	"	"	"	0.0054

Being under the impression that this loss was incurred by the co-precipitation (by fumaric acid) with thorium, of some compound, which, on ignition with the blast yielded a volatile oxide, it was thought advisable to prepare a quantity of thorium fumarate from thorium which had been precipitated with fumaric acid and thoroughly ignited. This was done in the following way:

The pure thorium solution was precipitated in the usual way with fumaric acid, and ignited for a period of one and one-half hours in the strongest heat that could be obtained from a blast

lamp. The thoria was again brought back into solution after many evaporations with concentrated sulphuric acid, precipitated with ammonia, filtered, redissolved in nitric acid, evaporated to dryness, taken up in water and reprecipitated with fumaric acid; thoroughly washed, and dried.

Combustions were then made on this compound as before:

	ThO_2	CO_2	*Ratio*	*Loss on ignition*
I	0.1870	0.1270	1 : 4.07	0.0066
II	0.2434	———	———	0.0073

The same white fumes were driven off on ignition with the blast, causing a corresponding decrease in the weight of thoria left after combustion.

To learn whether the white fumes were a carbon-containing compound or not, the platinum tube was connected to the combustion furnace and then heated with a blast. No increase in weight was obtained in the soda-lime tube, showing the absence of carbon, but an increase, slightly greater than the loss in weight of thoria, was found in the water-absorption tube (pumice and sulphuric acid).

To find out whether the fumaric acid employed was pure and free from any non-volatile substance, several portions were burned at a gentle heat in a Bunsen flame; no residue was left. A combustion of the acid was also made giving:

	found	*calculated*
H	3.42	3.44
C	41.302	41.38

The fumaric acid was pure, and the white fumes obtained by the ignition of the thorium fumarate are as yet unaccounted for. These white fumes, however, will be made the subject of a separate investigation.

The only conclusion to be drawn from the above work is that the thorium and fumaric acid react molecule for molecule.

It is not supposed that the unsaturated valencies in the fumaric acid play any part in the reaction, but rather that fumaric acid is of just the proper strength to throw out the very feebly basic thorium.

MONAZITE ANALYSES.

To test the application of the fumaric acid to the analysis of monazite sand, three samples were procured: two Brazil sands, and one North Carolina,* and to check the results obtained, two of the best known methods (the thiosulphate and ammonium oxalate separations) together with a third,—a combination of the thiosulphate and oxalate—were employed.

A description of the methods used is as follows:

Ammonium Oxalate Separation.

About one gram of the sand, ground to an impalpable powder, was weighed out into a platinum vessel, covered over with 15-20 c.c. concentrated sulphuric acid, and evaporated on an asbestos board until fumes were no longer driven off. More sulphuric acid was added, and this repeated several times until the conversion of the phosphates into sulphates was complete.

This mass was then projected in very small quantities into about 700 c.c. water at 0° C with constant agitation (the temperature was not allowed to rise above 2° C.) This was allowed to stand several hours with frequent stirring, filtered and washed.† The filtrate was then nearly neutralized with dilute ammonia (1 : 20) and 50 c.c. of a cold saturated solution of oxalic acid added, (for each gram of ore taken) stirred well, and allowed to stand. After the heavy white precipitate had settled completely, the solution was filtered, washed, and the precipitate washed into a 400 c.c. beaker, using a cold saturated solution of ammonium oxalate for the purpose. After making the volume of ammonium oxalate equal to about 50 c.c. the beaker was placed on a water-bath, covered with a watch glass, and digested for one and one-half hours with occasional stirring. This was then diluted to 300 c.c. and allowed to stand over night; filtered (filtrate A) and washed. The resi-

(* It was through the kindness of Prof. Baskerville that we secured this sample of North Carolina sand.)

(† Preliminary experiments showed that no metals precipitable by hydrogen sulphide were present, so this part of the process was omitted.)

due was again subjected to the treatment with ammonium oxalate, &c., &c., and filtered (filtrate B).

Filtrates A and B were combined and precipitated by a large excess of ammonia; heated to boiling, filtered, and the thorium hydroxide dissolved off the filter in hot dilute nitric acid; evaporated to dryness, the residue taken up in water and precipitated with oxalic acid. This precipitate of thorium oxalate, which still contained some impurity, was again treated with ammonium oxalate as before (one treatment), precipitated with an excess of ammonia, converted into the oxalate, ignited and weighed as ThO_2.

Thiosulphate Method.

The mineral was decomposed and brought into solution as before, and precipitated with oxalic acid. The precipitate of oxalates was washed into a beaker and treated with a strong solution of caustic potash (about 25 c.c.); heated to boiling (this converts the oxalates into hydrates which are then quite soluble in acids), diluted, and filtered; washed thoroughly and dissolved off the filter in hot dilute hydrochloric acid (1 : 1); evaporated to dryness to free from acid, taken up in 75-100 c.c. water and 15 c.c. of a saturated solution of sodium thiosulphate added, and heated to boiling; (this precipitates nearly all the thorium together with a trace of impurity and considerable sulphur), filtered, (precipitate A) and the filter setaside for subsequent filtration. The filtrate was precipitated by an excess of ammonia, filtered, washed, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with thiosulphate as before. This was filtered through the paper containing precipitate A. The precipitation with thiosulphate was repeated, in the successive filtrates, as long as a precipitate was obtained (usually a third precipitation extracts the thorium completely).

The combined precipitates of thorium thiosulphate were washed completely, then dried and ignited. The ignited mass was fused several times with potassium bisulphate, taken up in water and a few drops of hydrochloric acid and precipitated with

oxalic acid. These oxalates were converted into the hydrates as before, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with sodium thiosulphate; filtered, washed, dried and ignited. This was again fused with bisulphate, dissolved in water and a few drops of hydrochloric acid, and precipitated with oxalic acid; filtered, washed, ignited and weighed.

It was necessary to fuse the thoria several times with bisulphate to get it all into solution.

Combination Method.

Inasmuch as the methods just described are very lengthy and involve very troublesome processes, such as the repeated digestion of a large bulk of oxalates with ammonium oxalate or the repeated fusions necessary in the thiosulphate method, it was found very convenient to make a combination of the two. Another point, well worth mentioning, and shortening the process greatly, is the conversion of the thorium thiosulphate back into the nitrate without ignition and repeated fusions. This is very easily and quickly done by washing the precipitate of thorium thiosulphate into a beaker with water, adding 20-25 c.c. of a strong solution of caustic potash and heating to boiling. The thorium is converted completely into the hydrate, while at the same time any free sulphur is dissolved by the caustic potash. The mass then is simply brought to boiling, diluted, filtered, washed, and dissolved off the filter in dilute nitric acid.

As has been noticed, the same reagent (caustic potash) serves for the conversion of the oxalates into hydrates which are then easily converted into the nitrates.

The combination method is as follows:

Decompose the mineral as usual and precipitate the rare earths as oxalates; filter, and wash the oxalates into a beaker; add 20-25 c.c. of a strong solution of caustic potash and heat to boiling; dilute, filter and wash. Dissolve the hydrates off the filter with hot dilute hydrochloric acid (1 : 1) and evaporate to dryness on a water bath. Take up with water and add 25-30 c.c. of a saturated solution of sodium thiosulphate; heat

to boiling, filter and wash (precipitate A) and set the filter aside for subsequent filtration. Precipitate the filtrate with an excess of ammonia, filter, wash, dissolve off the filter with hot dilute hydrochloric acid and evaporate to dryness. Take up with water and reprecipitate with thiosulphate as before. Filter this precipitate through the paper containing precipitate A. Wash, then wash into a beaker and add 20-25 c.c. of a strong solution of caustic potash and heat to boiling. Dilute, filter and wash. Then dissolve off the filter in warm dilute nitric acid and evaporate to dryness. Redissolve in water and precipitate with oxalic acid; filter, wash, and rinse into a beaker using a cold saturated solution of ammonium oxalate for the purpose (about 100 c.c.)* Digest this on a water bath for one and one-half hours (covered with a watch glass), dilute to 300 c.c. and allow to stand over night. (The undissolved residue of Ce, La, Di, &c., is so slight that it need not be re-treated.) Filter and precipitrate the thorium from the filtrate with a large excess of ammonia. Filter, dissolve in dilute nitric acid, evaporate to dryness, take up in water and precipitate the thorium from this with oxalic acid. Filter, wash, ignite and weigh.

The above method gives very satisfactory results and yields a white oxide of thorium.

Fumaric Acid Method.

The three methods just described are very long and tedious. In many instances the solutions must be allowed to stand over night, and the precipitations repeated several times to insure a complete separation. The minimum time required to execute any one of these methods is from five to six days.

The method about to be described has the great advantage of being extremely short, requiring only about one and one-half days after the decomposition of the mineral, and gives accurate results. The method is as follows:

Decompose about one gram of mineral as before and precipi-

(* By this process the oxalate to be digested with ammonium oxalate is almost pure thorium oxalate and goes into solution very easily. Usually only the faintest residue of impurities remains after one digestion.)

tate the oxalates; wash, then rinse into a beaker and add 20-25 c.c. of a strong solution of caustic potash; heat to boiling, dilute, filter and wash. Dissolve off the filter in warm dilute nitric acid (1 : 1) and evaporate to dryness on a water bath. Take up in 50 c.c. water, then add alcohol and water in such proportions as to make the solution 40% alcohol (dilution = about 200 c.c.) Then add 20-25 c.c. of fumaric acid (0.1 gr. per 10 c.c.) and heat to boiling. Filter, while still hot, through a long-stem funnel (or by suction), wash several times with hot 40% alcohol, then return precipitate and paper to the beaker and add 25-30 c.c. of dilute hydrochloric acid (1 : 1); heat to boiling, dilute a very little, (keep down the volume as much as possible) and filter off the paper. Wash the paper several times, then evaporate to dryness on a water bath, shaking from time to time and washing with a few drops of water to prevent the residue from clinging to the sides of the beaker. Add about 50 c.c. water (while still on the water-bath) and stir the residue loose from the bottom with a rubber-capped rod. (The carbonaceous matter from the partly decomposed fumaric acid, &c., does not interfere). Add alcohol and water to make the solution 40%, (dilution about 150 c.c.) then add about 10 c.c. fumaric acid and heat to boiling. Filter through long-stem funnel, wash with hot 40% alcohol, ignite (without previous drying) in a platinum crucible, and weigh the ThO_2.

In this method hydrogen sulphide need not be passed through the solution before precipitation with oxalic acid, for, as has been shown on a preceding page, none of the metals precipitable by hydrogen sulphide interfere.

A comparison of the analyses of the three samples of sand, made by the methods described is given in the following table: Results are given in percentages of thoria.

	Methods.			
	Fumaric.	Oxalate.	Thiosulphate.	Combination.
Brazil (a).....	2.41 2.55	2.77 2.03	2.11	2.48
N. Carolina....	3.95 4.02 3.92			4.03 3.76
Brazil (b).....	2.51 2.47			2.42 2.56

Volatility of Chlorides of Rare Earths.

Drossbach * mentions a separation of thorium from its allied rare earths, based upon the volatility of their chlorides in a stream of chlorine gas. He does it by mixing the oxides with carbon, and then applying heat while a stream of chlorine gas is being passed over the mixture. The thorium being the most volatile, should be driven over, together with a small quantity of the other rare earths, which are subsequently separated by means of cuprous oxide, a method proposed by Boisbaudran.

If the thorium could be completely driven over, this would be a convenient means of preparing a relatively pure thorium, and it was to test this point that the work was repeated.

Carbon (prepared from pure starch) was very thoroughly mixed with pure thoria, placed in a porcelain boat, and then introduced into a hard glass tube. Well dried chlorine gas was passed through and the heating begun.

At a comparatively low heat, (long before dull redness) white fumes passed off which were insoluble in water, but could be readily absorbed in alcohol. From this solution in alcohol a white precipitate can be obtained by adding ammonia.

Berzelius,† one of the earliest investigators in this line, was the first to notice these white fumes.

* *Jour. f. Gasbel*, (1895.)

† Pogg. Ann. (1829), 16, pg. 403.

However, these vapors were not investigated farther since Baskerville * has reserved the investigation for himself.

By increasing the heat, thorium tetrachloride began to sublime on the cooler parts of the tube, but a considerable quantity remained behind in the boat, which could not be driven over even with the most intense heat (all the tube would allow).

A mixture of the oxides of cerium, lanthanum and didymium oxides was also made and treated in the same way as the thoria, and it was found that quite an appreciable quantity of their chlorides (or oxychlorides) was sublimed on the cooler parts of the tube.

* J. A. C. S. XXIII, 761.

CONCLUSIONS.

1. A saturated solution of fumaric acid in 40% alcohol precipitates thorium completely from neutral solutions, to which 40% of their volume of alcohol has been added, while under these conditions the only other metals that give precipitation are zirconium, erbium, silver, and mercury.

2. This precipitation serves as an accurate and rapid separation of thorium from the other earths in monazite, and by its use the thoria can be determined in about one-third the time heretofore required, and with equal if not greater accuracy.

3. As the thorium-carbon ratio in thorium fumarate is 1 : 4, thorium and fumaric acid react molecule for molecule.

4. By the aid of a blast lamp, white vapors are driven off from the thoria left in the boat after the combustion of thorium fumarate in a stream of oxygen (a fact as yet not explained).

5. Rare-earth oxalates, and thorium thiosulphate are completely converted into the hydroxides by heating to boiling in a strong solution of potassium hydroxide, giving a convenient method for the conversion of those salts into the nitrates.

6. Thorium cannot be quantitatively driven out of a mixture of rare-earth oxides by mixing with carbon and heating in a stream of chlorine gas.

BIOGRAPHICAL.

Floyd J. Metzger entered Buchtel College at Akron, O. in September, 1895 and was graduated in June, 1899, receiving the degree of Ph.B. Entered the University of Pennsylvania in October, 1899, and remained there till June, 1900, doing graduate work in chemistry. Entered the Sheffield Scientific School of Yale University in October, 1900, pursuing graduate work in chemistry until June, 1901. October, 1901, to June, 1902, studied for the degree of Ph.D. under the Faculty of Pure Science at Columbia University.

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